

AD-A138 551 CHEMICAL PROPERTIES AND FILM CASTING OF RADIATION
GRAFTED ION-CONTAINING.. (U) TEXAS A AND M UNIV COLLEGE
STATION DEPT OF CHEMISTRY M N SZENTIRIMAY ET AL

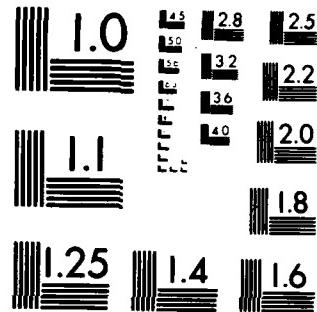
UNCLASSIFIED 27 FEB 84 TR-3 N00014-82-K-0612

F/G 11/9

1//

NL

END
DATE FILED
4-84
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A138551

OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

Task No. NR 627-838

TECHNICAL REPORT NO. 3

1.2

Chemical Properties and Film Casting of Radiation
Grafted Ion-Containing Polymers

by

Marilyn N. Szentirmay and Charles R. Martin

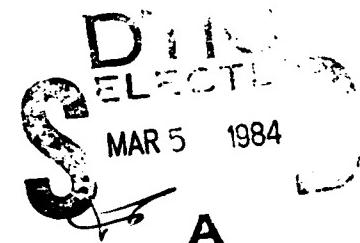
Prepared for Publication

in the

Journal of the Electrochemical Society

Department of Chemistry
Texas A&M University
College Station, Texas

February 27, 1984



Reproduction in whole or in part is permitted for
any purpose of the United States Government

ONC FILE COPY

* This document has been approved for public release
and sale; its distribution is unlimited

* This statement should also appear in Item 10 of Document Control Data
- DD Form 1473. Copies of form available from cognizant contract
administrator.

84 03 02 002

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 3	2. GOVT ACCESSION NO. AD-A138 551	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CHEMICAL PROPERTIES AND FILM CASTING OF RADIATION GRAFTED ION-CONTAINING POLYMERS		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Marilyn N. Szentirmay and Charles R. Martin		8. CONTRACT OR GRANT NUMBER(s) N00014-82K-0612
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Texas A&M University College Station, Texas 77843		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 627-838
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217		12. REPORT DATE February 23, 1984
		13. NUMBER OF PAGES 28
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Presented at the Rocky Mountain Conference, Denver, Colorado, July, 1983.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Ionomer Membranes, Polymer Films, RAI pore Membranes, Polyelectrolytes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A series of radiation grafted cation and anion exchange polymers have been studied with the intent of developing procedures for dissolving and film casting these polymers. Solvent swelling studies have shown that these polymers display two maxima in plots of solvent uptake vs. solvent solubility parameter. While similar behavior is shown by the ion exchange polymer Nafion, the anion and cation exchange polymers studied here will not dissolve under conditions (developed by us) which dissolve Nafion. We		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT (continued)

believe this insolubility results from covalent cross links and/or enhanced crystallinity in the chain material regions of these polymers. These polymers, do however, swell extensively in certain solvents at high temperatures and suspensions may be prepared from the swollen polymer. We have cast films from these suspensions onto electrode surfaces and report initial results of electrochemical characterization of these films.



tion

ability fades
with and/or
experience.

A-1

S/N 0102-LP-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

**Chemical Properties and Film Casting
of Radiation Grafted Ion-
Containing Polymers**

Marilyn N. Szentirmay and Charles R. Martin*

**Department of Chemistry
Texas A&M University
College Station, Texas 77843**

***Electrochemical Society Active Member.**

Abstract

A series of radiation grafted cation and anion exchange polymers have been studied with the intent of developing procedures for dissolving and film casting these polymers. Solvent swelling studies have shown that these polymers display two maxima in plots of solvent uptake vs. solvent solubility parameter. While similar behavior is shown by the ion exchange polymer Nafion, the anion and cation exchange polymers studied here will not dissolve under conditions (developed by us) which dissolve Nafion. We believe this insolubility results from covalent cross links and/or enhanced crystallinity in the chain material regions of these polymers. These polymers do, however, swell extensively in certain solvents at high temperatures and suspensions may be prepared from the swollen polymer. We have cast films from these suspensions onto electrode surfaces and report initial results of electrochemical characterization of these films.

Introduction

Ion-containing polymer, (ICP) (1,2), membranes have been used as separators in chlor-alkali cells (3) and in cells for energy conversion (4,5), and ICP film-based chemically modified electrodes show promise for use in electrochromics (6), electrocatalysis (7), photo-electrochemistry (8) and electroanalysis (9,10). Further developments in these areas will require ICPs with better mechanical and dynamic properties (11) which can be produced at a lower price (12). Accordingly, this research group has been investigating the fundamental chemical and electrochemical properties of a variety of ICPs (13,14) and studying possible new applications for these polymers (10,15).

We report at this time results of studies of ICPs prepared by derivitizing, through radiation grafting, polyethylene (PE) and polytetra-fluoroethylene (PFE) sheets (12,16). Both cation exchange polymers (sulfonated PEs and PFEs) and anion exchange polymers (quaternized PEs and PFEs) were studied. These polymers are of interest because they may prove to have the desirable chemical and transport properties of Nafion, a highly successful perfluorosulfonate polymer (1,13,14), but can be produced at lower costs (12). The quaternized polymers are of particular interest to us because they may prove to be cationic versions of Nafion and thus be useful when anion exchange or transport is needed.

The purposes of the work described here were to use solvent swelling studies (12,17) to develop procedures for film casting these radiation grafted ICPs and to use electrochemical methods for preliminary investigations of the physical and transport properties of the resulting films. Particular emphasis is placed on the quaternized polyethylene polymer.

Experimental

Materials. The ICPs and polyethylene were obtained from RAI Research Corporation (Hauppauge, NY). The sulfonated polyethylene (PE-SS, 700 g/mole -SO₃H) and the sulfonated polytetrafluoroethylene (PFE-SS, 850 g/mole -SO₃H) are prepared by grafting styrene onto sheets of the polymer, followed by sulfonation of the styrene (12,16). The quaternized polyethylene (PE-QA, 1100 g/mole N) and the quaternized polytetrafluoroethylene (PFE-QA, 1000 g/mole N) are prepared by grafting vinylbenzylchloride onto the polymers and quaternized with triethylamine (16). Membranes were converted to various counterionic forms by soaking in appropriate salt or acid solution.

Water was triply distilled or obtained from a Milli-Q water purification system (Millipore Corp., Bedford, MA). 2-Ethylhexanol, 1-decanol, 2-ethylbutanol, 1-pentanol, ethylene glycol, sodium anthraquinone-2-sulfonate, disodium anthraquinone-2,6-disulfonate, and sodium hexafluorophosphate were obtained from Aldrich Chemical Co. (Milwaukee, WI). Xylene was obtained from Center Chemical Co. (Austin, TX). Triethylamine was obtained from MCB (Cincinnati, OH). Hydroquinone was obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ). Trifluoroacetic acid (TFA) was obtained from Sigma Chemical Co. (St. Louis, MO). Ru(NH₃)₆Cl₃ was obtained from Johnson Matthey, Inc. (Winslow, NJ). 8-Hydroxy-1,3,6-pyrenetrisulfonic acid, trisodium salt was obtained from Eastman Kodak Co. (Rochester, NY) and recrystallized twice from aqueous acetone. Ru(bpy)₃Cl₂ (bpy=2,2'-bipyridine) was obtained from G. F. Smith. All other chemicals were reagent grade.

Solvent Swelling Measurements. Studies similar to those described by Yeo, et al. (12,17) were done. The membranes (0.06-0.10 g) were immersed in the

desired solvent in a capped vial at room temperature for at least two days, then removed, blotted dry, and weighed immediately in a closed weighing bottle. The membranes were then replaced in the solvents and re-weighed more than one day later to insure that no further solvent uptake had occurred. Each value of % increase in weight is the average of two or more experiments. In almost all cases, reproducibility was better than $\pm 5\%$.

Preparation of Polymer Suspensions. Specific conditions used to soften the ion exchange polymers are given in the Results and Discussion section. The pressure reactor (Parr Instrument Co., Moline, IL) was purged with N_2 before sealing. In some cases, N_2 was added after sealing to increase the pressure in the reactor. The contents of the reactor were stirred while heating. Prior to heating in the reactor, PFE-SS was ultrasonically cleaned in 50:50 ethanol-water to remove a pink color. The softened polymers were ground in a glass tissue grinder driven by an overhead stirring motor. Titrations to check the manufacturers listed value of the ion exchange capacity of PE-QA (chloride form) were done by equilibrating a known weight of polymer with aqueous KNO_3 and titrating the Cl^- released with $AgNO_3$. Chlorofluorescein was used as the indicator.

Preparation of Electrode Films. Glassy carbon (1/8 in. diameter, Atomergic Chemetals Corp., Plainview, NY) was polished as described previously (14). Films of PE-SS and PE-QA were cast onto glassy carbon electrodes from suspensions in propanol, PFE-QA from a suspension in 50:50 ethanol-water, and PFE-SS from a suspension in 50:50 ethylene glycol-ethanol. The electrodes were coated by syringing a measured amount of polymer suspension onto the electrode surface (14). After the solvent evaporated (in air), the polymer-coated electrodes were soaked at least 6 hr in supporting electrolyte before use. This served to both hydrate the film and wash out any residual solvent. Wet film thicknesses were measured with an Alpha-step surface

profiler (Tencor Instruments, Mountain View, CA).

Electrochemical measurements. A PAR Model 174 potentiostat and Model 175 programmer (EG & G PAR, Princeton, NJ), an X-Y recorder (Houston Instruments, Austin, TX) and a Nicolet 2090-3 digital oscilloscope (Nicolet Instrument Corp., Madison, WI) were used for electrochemical experiments. A three-electrode cell with a saturated calomel reference electrode (SCE) and a Pt disk counter electrode was employed. All electrochemical measurements were done in N₂-degassed solutions.

Results and Discussion

Solvent Swelling Studies. Yeo, et al. (12,17) have found that Nafion and the sulfonated RAI membranes exhibit two maxima in plots of solvent uptake vs. solvent solubility parameter. We have shown that Nafion may be dissolved at high temperatures in binary solvent systems composed of a solvent which has a solubility parameter near the first swelling maximum and a solvent which has a solubility parameter near the second swelling maximum (13). It was of interest to us to see if a similar approach could be used to dissolve the various RAI membranes. If so, chemically modified electrodes based on films of these polymers could be prepared. Such electrodes allow for convenient evaluation of the charge transport properties (14) and the ion exchange thermodynamics (10) of ICPs.

Solvent swelling studies are also of interest because they can be used to deduce information about ICP morphology (*vide infra*). Solvent swelling data are already available for the sulfonated RAI polymers (12). We report results of swelling studies of PE-QA. Since the solvents used varied in hydrogen bonding ability, three component solubility parameters (δ) (18,19) were used for these studies. The solvents and their solubility parameters are listed in Table I.

Results of the solvent swelling studies of PE-QA are shown in Figures 1-3. In pure solvents, the Cl^- form of PE-QA exhibits two swelling maxima, one at approximately 10 δ , the other a broad maximum in the range 15-20 δ (Figure 1). As noted above, similar results were obtained with Nafion (17), PFE-SS and PE-SS (12). In propanol-water mixtures, PE-QA chloride exhibits solvent uptakes greater than those observed in either pure propanol or pure water (Figure 2). Again, this type of behavior was also observed with Nafion (17). Finally, when PE-QA is converted from the Cl^- form to the PF_6^- form its solvent swelling characteristics change dramatically (Figure 3). While nearly all of the solvents swell the PF_6^- form much less extensively, it is of particular interest to note that the low δ envelope is essentially completely wiped out.

It is now fairly well established that many ICPs are, on a microscopic level, biphasic (20). Yeo, et al. (12,17) have concluded that in Nafion, PFE-SS and PE-SS, the high solubility parameter envelope results from interactions in the ionic cluster phase (20) and the low solubility parameter envelope results from interactions with the organic chain material phase or with the sidechains. The fact that two δ maxima are observed in PE-QA Cl^- suggests that this ICP is also biphasic. Because polyethylene (the chain material in PE-QA) has a δ of about 8 (21) and the first swelling maxima occurs at $\delta = 10$, it is reasonable to conclude that the low δ maximum in PE-QA results primarily from interactions with the sidechains. A comparison of solvent uptake data for PE-QA with data for the polyethylene used by RAI to make PE-QA (Table II) supports this conclusion. The solvents which produce the greatest swelling in PE-QA do not appreciably swell polyethylene.

That the low δ maximum is attributable to interactions with the sidechains is also supported by the PF_6^- swelling data. It is generally

accepted that counterions are localized in the ionic domains of ICPs and not in the surrounding chain material phase (20). Therefore, if the swelling maximum at 10 Hb were due primarily to interactions with the chain material, the tremendous sensitivity of swelling to the nature of the counterion would not be expected. Furthermore, by the same argument, since the sidechain interactions are very sensitive to counterion, it seems likely that the sidechains intrude into the ionic domains. This intrusion of organic sidechain explains why luminescence probe studies of these ICPs indicate that the cluster phase is rather hydrophobic (22,23).

Polymer Suspensions. The swelling studies revealed several solvents and solvent systems which showed promise for dissolving PE-QA chloride (e.g., 50:50 ethanol water and dimethylsulfoxide). However, PE-QA would not dissolve in any solvent or solvent system, even at high temperatures and pressures. The failure of PE-QA to dissolve is surprising, since a similar approach was successfully used to dissolve Nafion (13). Since cluster formation may be regarded as electrostatic cross-linking (24), it seemed possible that the clusters might be responsible for the insolubility. To test this possibility, PE-QA chloride membranes were immersed for several hours in boiling xylene. This caused the charged sites to cleave from the membrane.* The uncharged membranes were then boiled in fresh xylene for several more hours. While boiling xylene will dissolve the polyethylene used to prepare PE-QA, it did not dissolve the decharged PE-QA. This shows that the presence of the charged groups (and, therefore, cluster formation) is not responsible for the insolubility. We believe that covalent cross-

*When as-received membranes are immersed in an aqueous solution of the fluorescent anion 8-hydroxy-1,3,6-pyrenetrisulfonate, strong fluorescence from the cationic membrane is observed. After treatment in boiling xylene, and reimmersion in the fluorophore solution, no fluorescence can be detected from the membrane.

links are introduced during the radiating grafting procedure; even a minute amount of cross-linking would render this polymer insoluble in any solvent.

We were also unable to dissolve PE-SS, PFE-QA and PFE-SS. PE-SS is probably also covalently cross-linked but tetrafluoroethylene polymers show little tendency to cross-link when bombarded with radiation (16). The insolubility of these polymers in solvent systems which will dissolve Nafion may result from higher degrees of crystallinity in the starting PFEs than in Nafion. The Nafions which we successfully dissolved (13) by heating to 250°C have melting points around 210°C (25). The melting point of the polytetrafluoroethylenes are around 350°C (26). While in principle this indicates that PFE-QA and PFE-SS could be dissolved at higher temperatures, we have found that in the solvents studied here the charged sites begin to cleave from PFE-QA at temperatures above about 150°C and from PFE-SS at temperatures above about 300°C.

In spite of their insolubility, we were able to cast films of all of these ICPs. This was accomplished by using the solvent swelling experiments to identify strongly swelling solvents, using these solvents in the high temperature reactor to soften the polymers, and then grinding the wet, softened polymer in a ground glass tissue grinder. Suspensions of the polymers resulted; these suspensions were filtered to remove the larger particles and then used to cast films. The conditions required to soften each polymer are shown in Table III. As noted above, temperatures high enough to soften PFE-QA also cleaved the charged sites. For this reason, we were forced to use lower than optimal temperatures, and poor softening resulted.

A comparison of the ion exchange capacities of PE-QA chloride before treatment and after suspension showed that charged sites are not destroyed during the softening and grinding process. The ion exchange capacities were 0.95 meq./g for the as-received membranes and 0.94 meq./g after suspension.

Polymer-Coated Electrodes. Films cast from the ICP suspensions were examined with a surface profilometer. These studies showed that, while the entire electrode surface was covered, the coatings were uneven, as might be expected for films composed of small adhering particles. Thickness measurements on wet PE-QA films gave densities of 0.69 g/cm^3 ; the density of the dry, as-received membrane is 0.65 g/cm^3 (27). Figure 4A shows background currents observed at a bare glassy carbon electrode. Figures 4B through E show analogous background currents for electrodes coated with the various RAI polymers. As would be expected (13), background currents do not change appreciably after coating.

As has been observed with other ICP-based chemically modified electrodes (13,28,29), the RAI films incorporate and retain electroactive counterions and allow for charge transport to and from these ions. For example, Figure 5A shows a series of cyclic voltammograms recorded after a PE-QA coated electrode was immersed in a solution of anthraquinone sulfonate (AQS). Current increased with time, eventually reaching a steady state level (13,28,29). When the electrode was removed from solution, rinsed, and placed in supporting electrolyte, current due to the retained AQS was observed. Voltammogram 5B was recorded 35 min after the coated electrode was placed in supporting electrolyte. While when immersed in supporting electrolyte, AQS is slowly leached from the polymer, the film itself remained attached to the electrode and could be reloaded with AQS to

the same voltammetric current level shown in the last scan in Figure 5A. Analogous results were obtained with the other RAI polymers.

Preliminary investigations of the charge and mass transport properties of PE-QA films at electrode surfaces were also carried out. Figure 6A shows that voltammetric peak currents, i_p , for polymer-bound AQS are proportional to the square root of scan rate. This is the expected (28) dependency in the thick (ca. 4 μM) films used here. Potential step chronocoulometry for AQS and anthraquinone-2,6-disulfonate (AQDS) in PE-QA films produced linear charge vs. $t^{1/2}$ plots (Figure 6B). Apparent diffusion coefficients (14,28) of about $1 \times 10^{-9} \text{ cm}^2/\text{s}$ were obtained, from such plots, for both the oxidized and reduced forms of AQS and AQDS.

Figures 5 and 6 show that PE-QA extracts and transports electroactive counterions. It was also of interest to evaluate the extent to which neutrals and coions permeate the film. We have found that small, neutral molecules (e.g., hydroquinone) readily penetrate films of PE-QA; in fact, peak currents for hydroquinone at coated electrodes are identical to those at uncoated electrodes. These molecules are not, however, retained by the film in that no trace of the hydroquinone voltammetric wave is observed when a PE-QA modified electrode is transferred from a hydroquinone solution to a solution containing only supporting electrolyte.

Coions (e.g., $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{NH}_3)_6^{3+}$) also penetrate PE-QA films. Peak currents for these ions are, however, reduced to less than about 25% of the peak currents observed for the same solution at an uncoated electrode. Coions are also not retained by these films. The ability of coions to penetrate the rather thick (4 μM) films used here suggests that there are pinholes or channels through the films. Again this is not surprising given the fact that these films are composed of adhering particles. We are

currently investigating the possibility of using annealing procedures to reduce the void volumes of these films.

Conclusions

Solvent swelling studies have provided a method for film casting the RAI ICPs. While these polymers show solvent swelling characteristics very similar to Nafion, they will not dissolve in solvents which dissolve Nafion (e.g., 50:50 ethanol-water (13), dimethylsulfoxide (29), propylene carbonate (30)). We suggest that cross-linking introduced during the grafting procedure or enhanced crystallinity cause this lack of solubility. The solvent swelling studies have also provided information about the polymer-solvent interactions which produce swelling and about the morphology of PE-QA. More importantly, these studies have shown that the chemical properties of the PE-QA ionomer are strongly dependent on the nature of the counterion.

Because of the ability to cast films, charge transport properties and ion exchange thermodynamics of these polymers may now be conveniently evaluated. In previous studies, we have shown that Nafion preferentially binds hydrophobic counterions (10,15,28) and that hydrophobic interactions can influence rates of diffusion in Nafion films at electrode surfaces (14). It will be of interest to see if hydrophobic interactions are of importance to ion exchange and charge transport in films of the RAI polymers.

Acknowledgements

This work was supported by the Office of Naval Research and by the Robert A. Welch Foundation.

References

1. A. Eisenberg and H. L. Yeager, Eds., Perfluorinated Ionomer Membranes, ACS Symposium Series No. 180, ACS, Washington, D.C. (1982).
2. A. Eisenberg, Ed., Ions in Polymers, ACS Advances in Chemistry Series, 197, ACS, Washington, D.C., (1980).
3. W. Grot, G. E. Munn and P. M. Walmsley, Presented to the 141st National Meeting of the Electrochemical Society, Houston, Texas, May 7-11 (1972).
4. F. G. Will, this Journal 126, 36 (1979).
5. A. B. La Conti, A. R. Fragala and J. R. Boyack, in, J. D. E. McIntyre, S. Srinivasan and F. G. Will, Eds., Proceedings of the Symposium on Electrode Material and Processes for Energy Conversion and Storage, the Electrochemical Society, Inc., N.J., 1977, p. 354.
6. K. Itaya, H. Akahoshi and S. Toshima, this Journal 129, 762 (1982).
7. K. N. Kuo and R. W. Murray, J. Electroanal. Chem. 131, 37 (1982).
8. N. Oyama, S. Yamaguchi, M. Kaneko and A. Yamada, J. Electroanal. Chem. 139, 215 (1982).
9. N. Oyama and F. C. Anson, J. Electrochem. Soc. 127, 247 (1980).
10. M. N. Szentirmay and C. R. Martin, Submitted, Anal. Chem.
11. B. R. Shaw, G. P. Haight, Jr. and L. R. Faulkner, J. Electroanal. Chem. 140, 147 (1982).
12. R. S. Yeo, S. F. Chan and J. Lee, J. Memb. Sci. 9, 273 (1981).
13. C. R. Martin, T. A. Rhoades and J. A. Ferguson, Anal. Chem. 54, 1639 (1982).
14. C. R. Martin and K. A. Dollard, J. Electroanal. Chem., In Press.
15. R. B. Moore, III, J. E. Wilkerson and C. R. Martin, Anal. Chem., Submitted.
16. V. D'Agostino, J. Lee and E. Lu, in, R. S. Yeo and R. P. Buck, Eds., Ion Exchange Transport and Interfacial Properties, The Electrochemical Society Remington, N.J., 1981, p. 148.
17. R. S. Yeo, Polymer 21, 432 (1980).
18. C. M. Hansen and A. Beerbower, in, Kirk-Othmer Encyclopedia of Chemical Technology, Supplemental Volume, 2nd ed., Wiley Interscience, N.Y. (1971), pp. 889-910.
19. C. M. Hansen and K. Skaarup, J. Paint Technology 39, 511 (1967).

20. T. D. Gierke and W. Y. Hsu, in, A. Eisenberg and H. L. Yeager, Eds., Perfluorinated Ionomer Membranes, ACS Symposium Series 180, ACS, Washington, D.C. (1982), pp. 283-307.
21. H. Burrell, in, J. Brandup and E. H. Immergut, Eds., Polymer Handbook, 2nd ed., John Wiley and Sons, N.Y. (1975), Chap. 4.
22. P. C. Lee and D. Meisel, J. Am. Chem. Soc. 102, 5477 (1980).
23. N. E. Prieto and C. R. Martin, in preparation.
24. S. C. Yeo and A. Eisenberg, J. Appl. Polym. Sci. 21, 875 (1977).
25. H. W. Starkweather, Jr. and J. J. Craig, Macromolec. 15, 752 (1982).
26. C. A. Sperati, in, J. Brandup and E. H. Immergut, Eds., Polymer Handbook, 2nd ed., John Wiley and Sons, N.Y. (1975), Chapter 5, p. V-32.
27. M. N. Szentirmay and C. R. Martin, Unpublished data, June 1983.
28. C. R. Martin, I. Rubinstein and A. J. Bard, J. Am. Chem. Soc. 104, 4817 (1982).
29. N. Oyama and F. C. Anson, J. Electrochem. Soc. 127, 247 (1980).
30. N. Oyama, T. Ohsaka, K. Sato and H. Yamamoto, Anal. Chem. 55, 1429 (1983).
31. C. R. Martin, Unpublished results, August 1983.

Table 1
Solvents and Solubility Parameters

Solvent	Solubility Parameter ^a (cal cm ⁻³) ^{1/2} , Hb
Triethylamine	7.4 ^b
Heptane	7.5 ^c
4-Methyl-2-pentanone	8.6
Xylene	8.8
2-Ethylhexanol	9.8
1-Decanol	10.0 ^c
2-Ethylbutanol	10.4
1-Pentanol	10.6
1-Butanol	11.3
1-Propanol	12.0
N,N-Dimethylformamide	12.1
Dimethylsulfoxide	12.9
Ethylene glycol	16.3
Formamide	17.8
Glycerol	21.1
Water	23.5

^aall values from reference (19), except as noted.

^bvalue from reference (21).

^cvalue calculated from reference (18).

Table 2

Solvent Uptake Measurements for Polyethylene and PE-QA

Solvent	% Increase in Weight	
	Polyethylene	PE-QA
Xylene	13	17
Decanol	2	60
Butanol	<1	42
DMSO	0	52
H ₂ O	0	42

Table 3
Summary of Conditions Used to Suspend RAI Polymers

Polymer	Counterion	Solvent	Temperature (°C)	Pressure (psi)	Time (hr)
PE-QA	Cl ⁻	50:50 Propanol-Water	150	100	4
PE-SS	Li ⁺	Methanol	150	250	4
PFE-SS	Li ⁺	Ethylene Glycol	250	730	3
PFE-QA ^a	OH ⁻	50:50 Propanol-Water	150	100	4

^avery little softening.

Figure Captions

Figure 1. Solvent uptake vs. solubility parameters of solvents for PE-QA, chloride form.

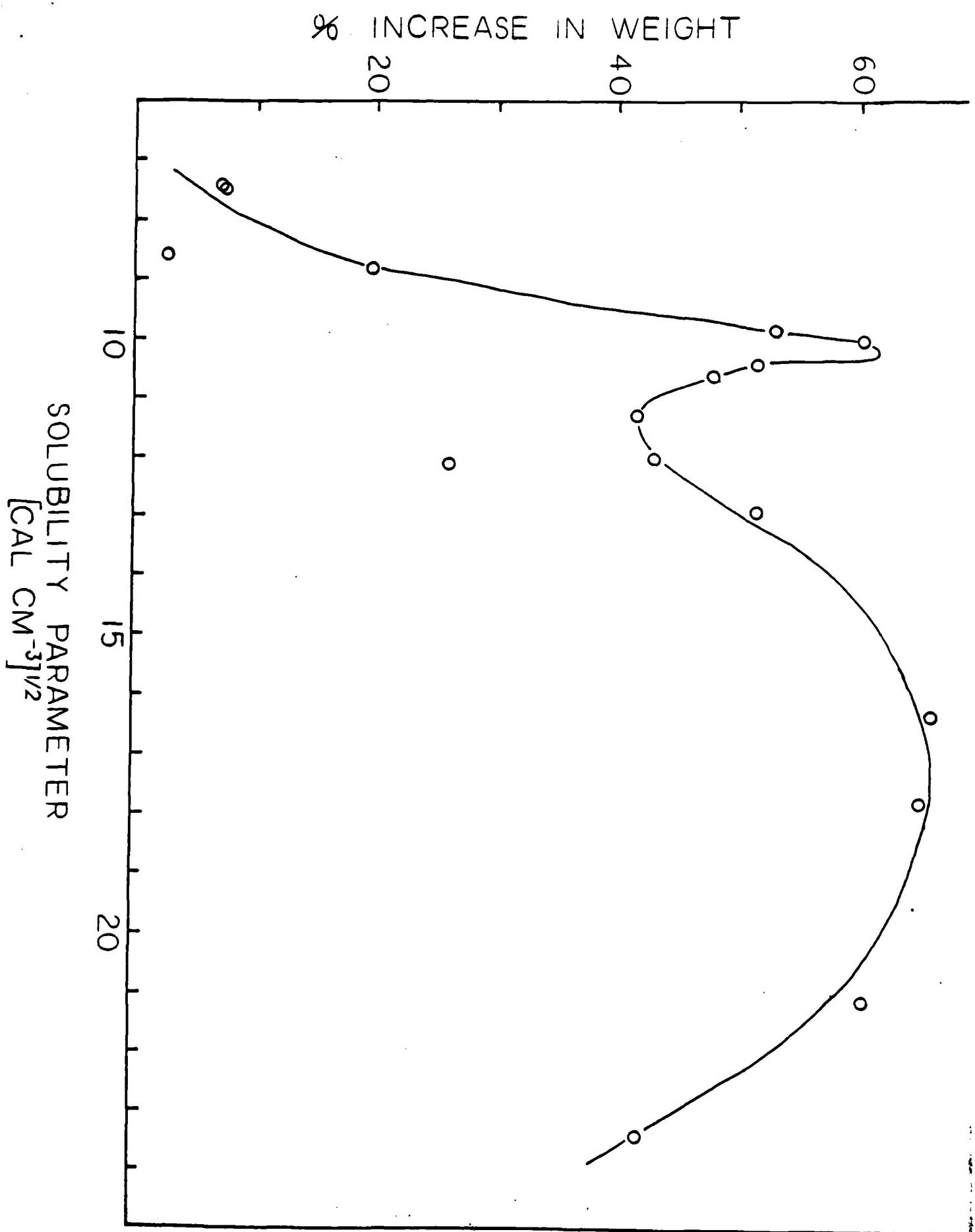
Figure 2. Solvent uptake of PE-QA, chloride form vs. solubility parameters, δ_{Mix} , propanol-water mixtures. $\delta_{\text{Mix}} = V_{\text{PrOH}} \delta_{\text{PrOH}} + V_{\text{H}_2\text{O}} \delta_{\text{H}_2\text{O}}$ (17), where V_{PrOH} and $V_{\text{H}_2\text{O}}$ are volume fractions, and δ_{PrOH} and $\delta_{\text{H}_2\text{O}}$ are solubility parameters, of propanol and water.

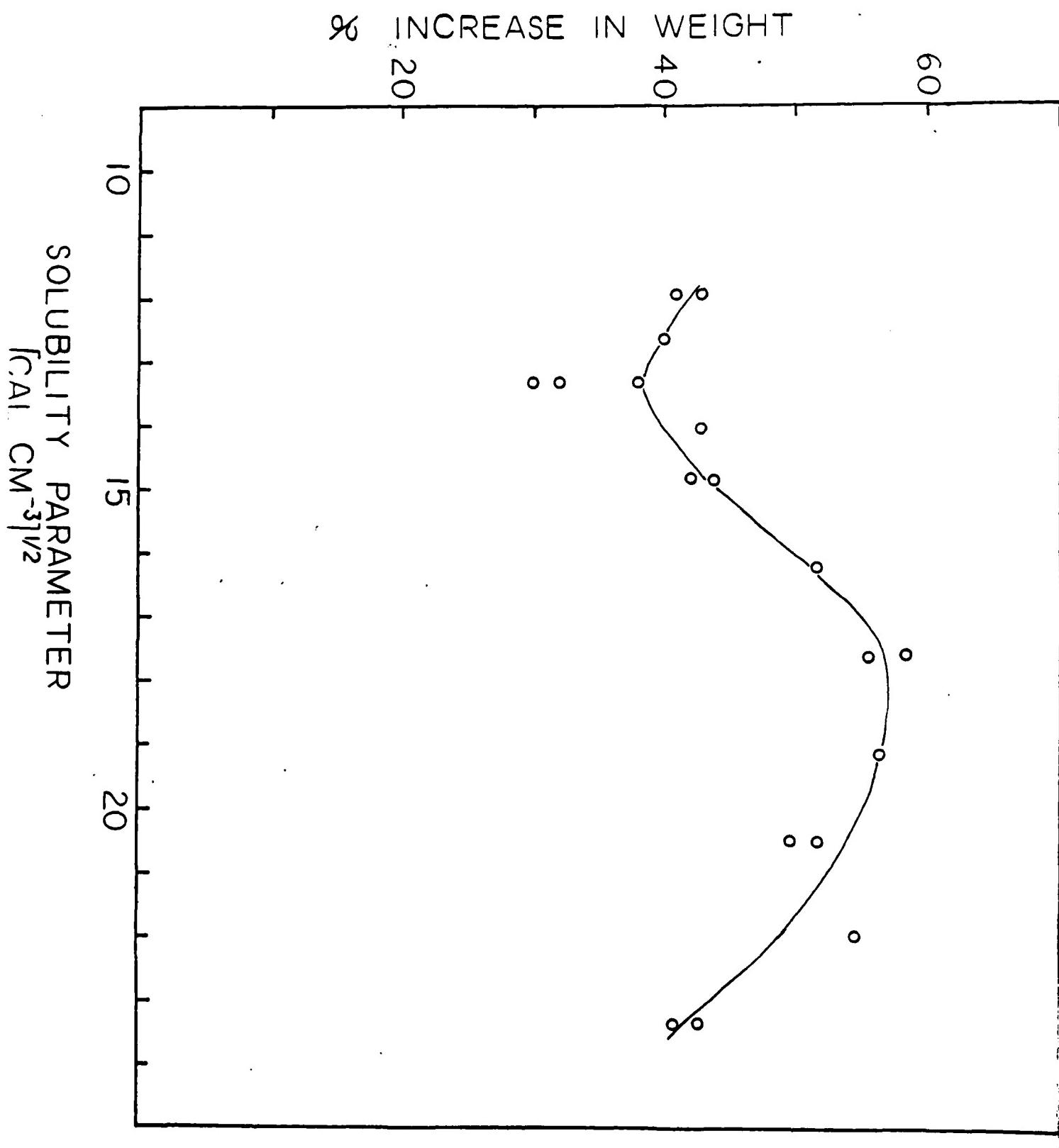
Figure 3. Solvent uptake vs. solubility parameters of solvents for PE-QA, PF_6^- form.

Figure 4. Cyclic voltammetric background currents recorded at 0.1 v/s.A.
Uncoated glassy carbon electrode in 0.2 M NaTFA, pH 3.0. B.-E. Glassy carbon electrodes coated with: B. PFE-SS, $\sim 10^{-7}$ moles $\text{SO}_3^-/\text{cm}^2$ (0.2 M NaTFA, pH 3.0).
C. PE-SS, 4.5×10^{-7} moles $\text{SO}_3^-/\text{cm}^2$ (0.2 M NaTFA, pH 3.0). D. PFE-QA,
 6.3×10^{-7} moles quaternary ammonium sites/ cm^2 (0.1 M TFA/0.1 M NaTFA).
E. PE-QA, 2.4×10^{-7} moles quaternary ammonium sites/ cm^2 (0.1 M TFA/0.1 M NaTFA).

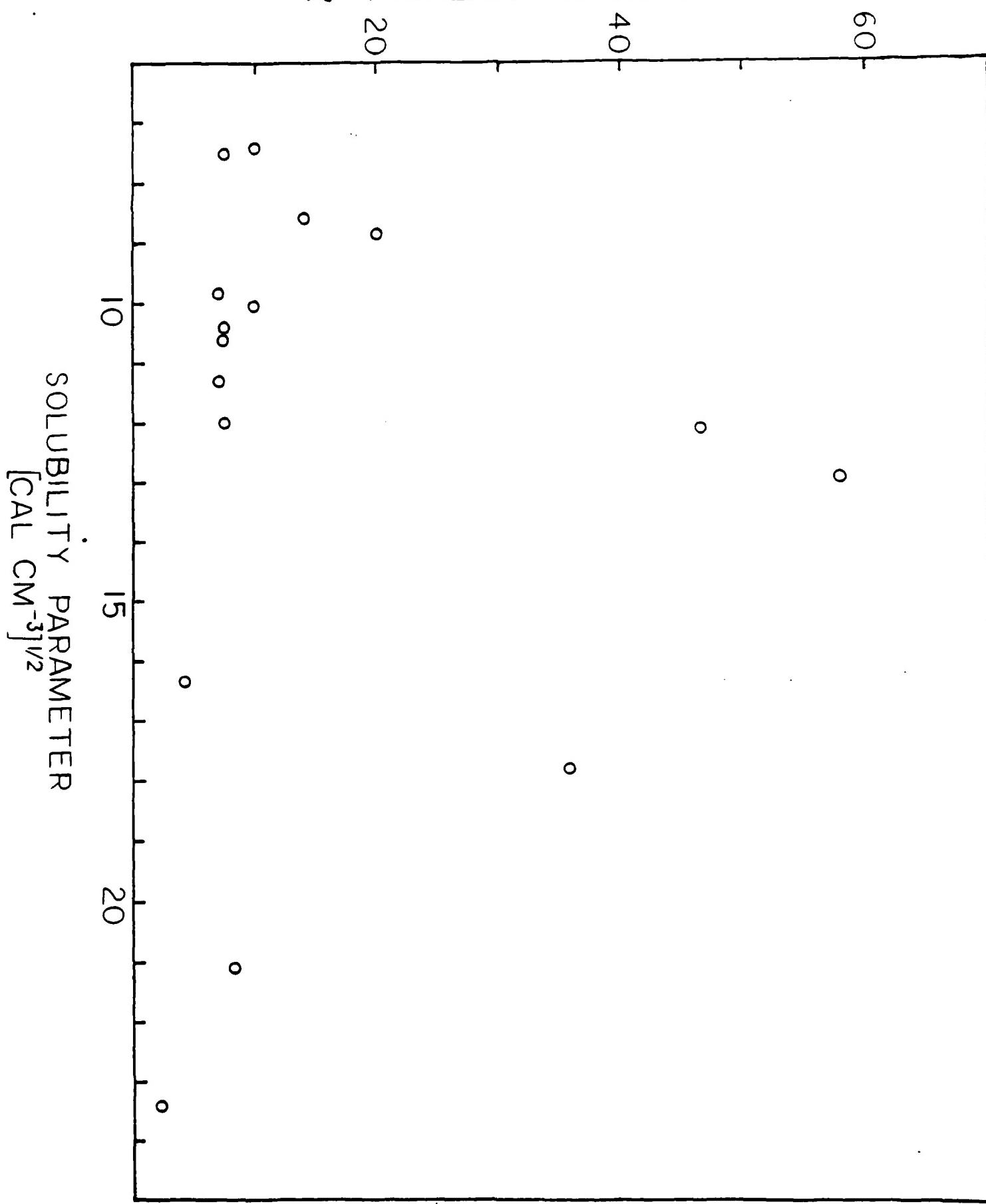
Figure 5. Cyclic voltammograms of AQS recorded at a scan rate of 0.1 v/s.
Supporting electrolyte = 0.2 M NaTFA, pH 3.0. A. Loading of PE-QA film
(4.5×10^{-7} moles quaternary ammonium sites/ cm^2 , 7 μm thick) from 2.3×10^{-4} M
AQS. First scan recorded immediately after immersion. Last scan recorded
1 hr 35 min later. B. Same PE-QA film after loading, rinsing and soaking in
supporting electrolyte for 35 min. C. Steady state voltammogram of
 2.3×10^{-4} M AQS on bare glassy carbon electrode.

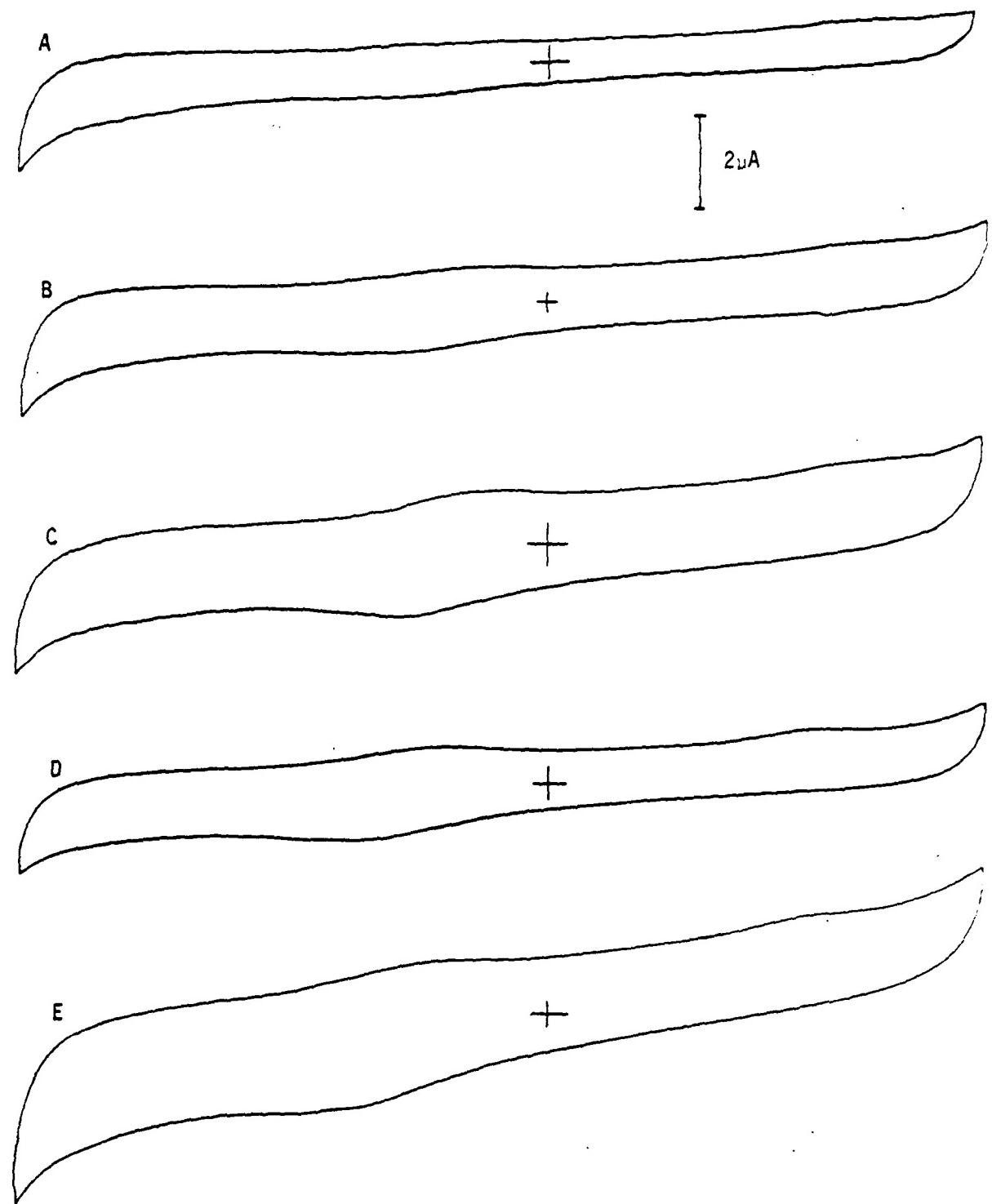
Figure 6. A. Anodic peak current, i_p , vs. square root of scan rate, $v^{\frac{1}{2}}$, for AQS in a PE-QA film (2.4×10^{-7} moles quaternary ammonium sites/cm², 4 μm thick). Supporting electrolyte: 0.1 M TFA/0.1 M NaTFA. B. Chronocoulometric plot of charge (Q) vs. $t^{\frac{1}{2}}$ for reduction of AQS in PE-QA electrode described in Figure 4D. Supporting electrolyte: 0.2 M NaTFA, pH 3.0.





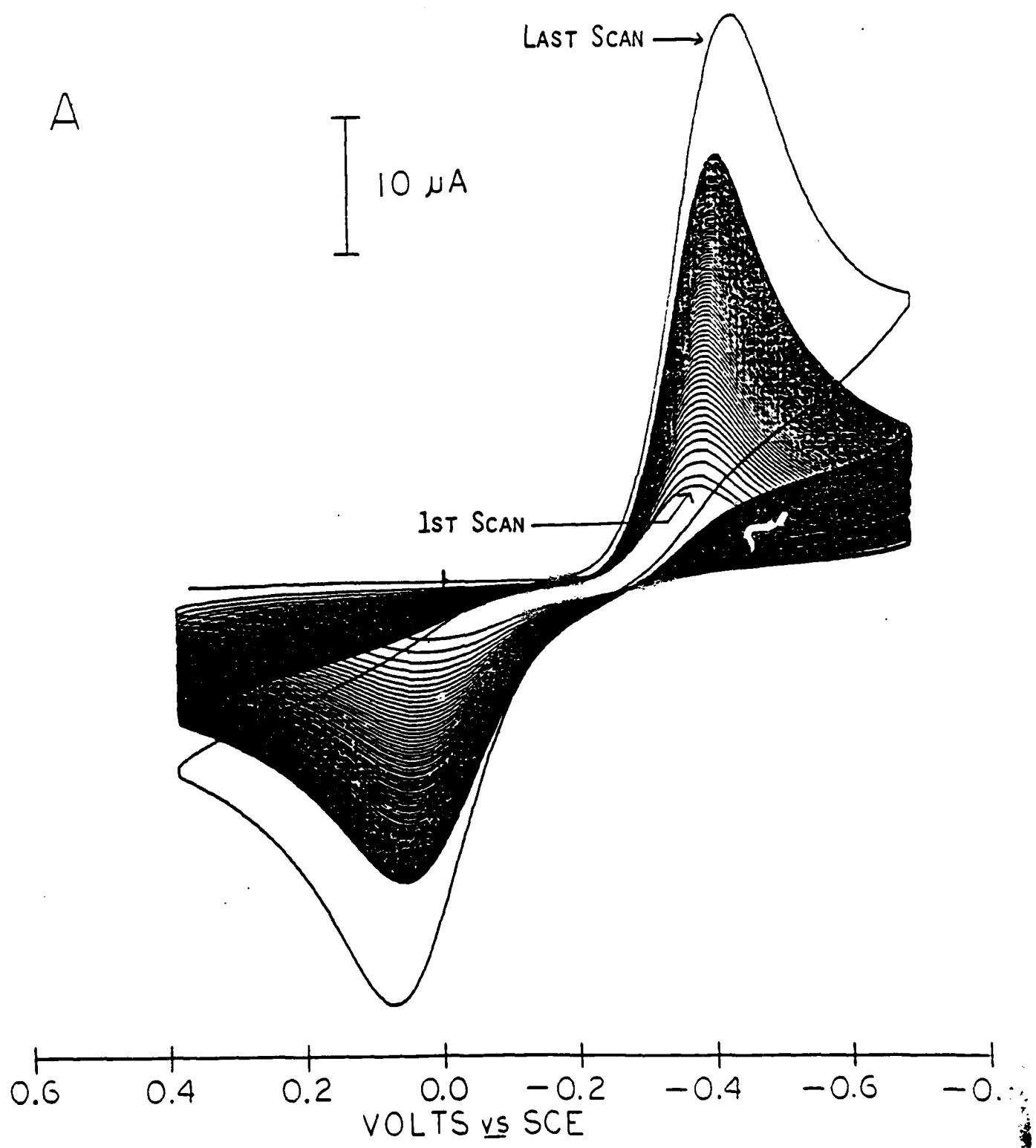
96 INCREASE IN WEIGHT

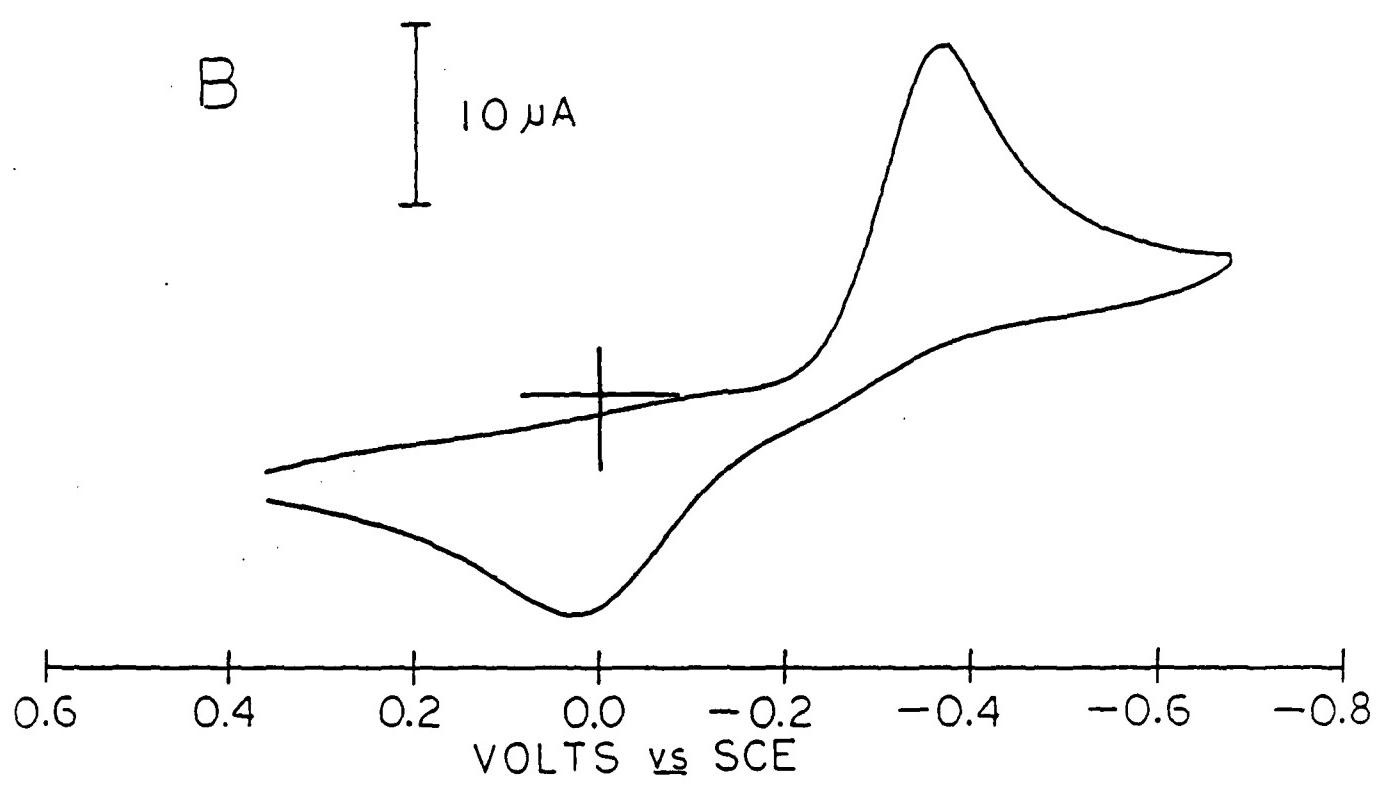


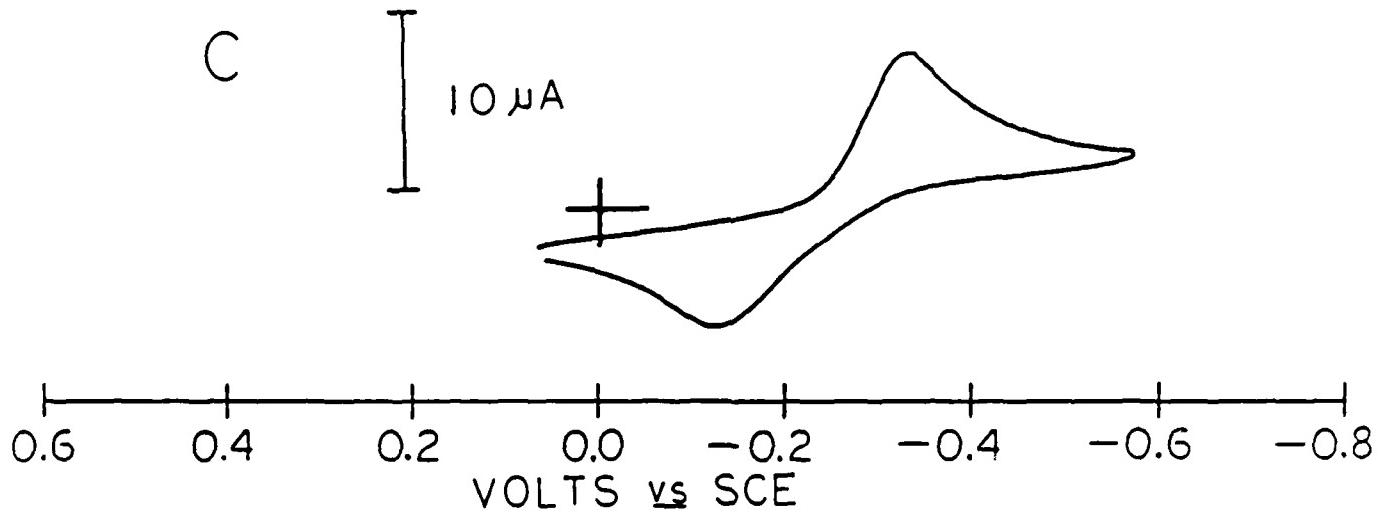


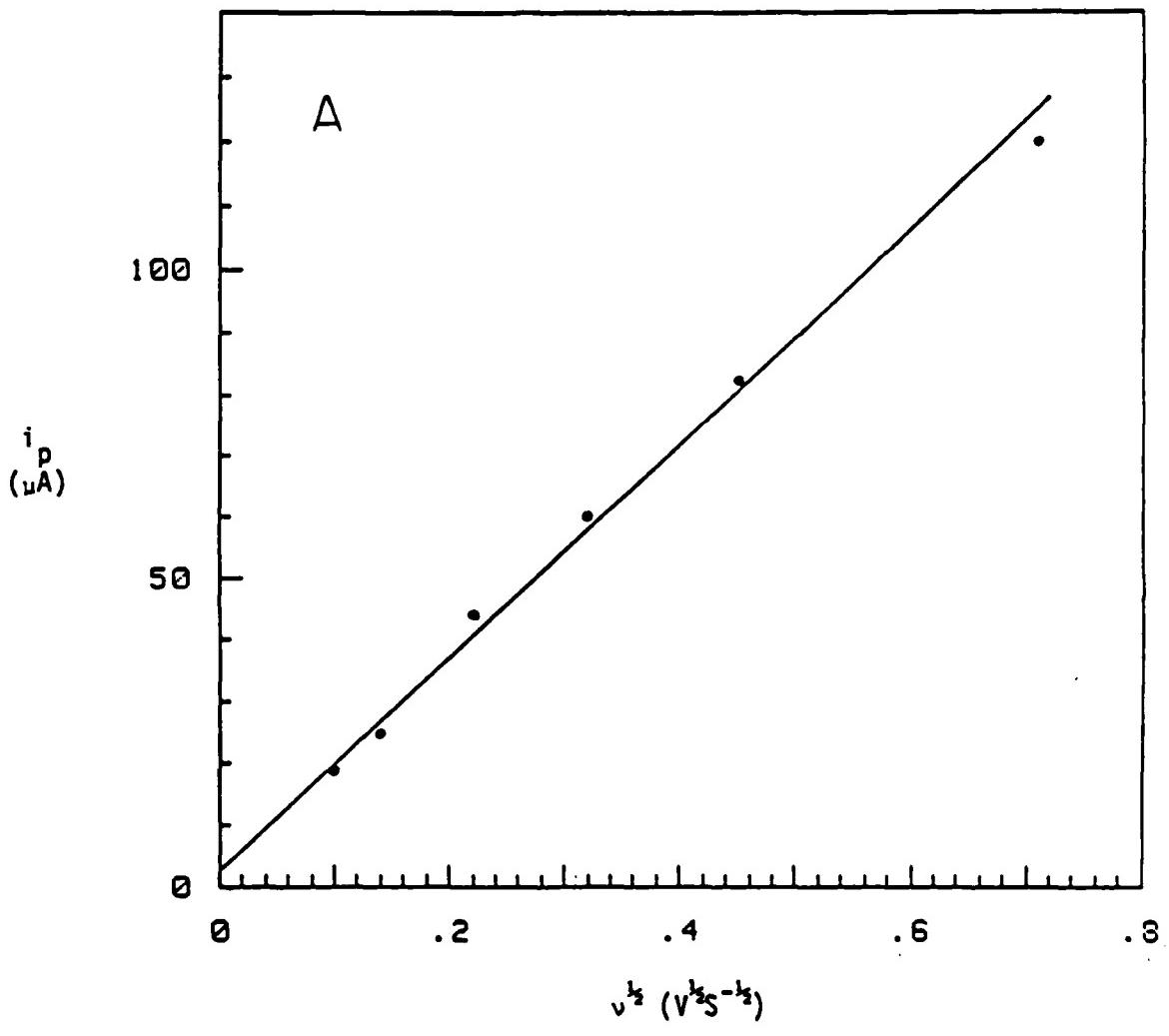
1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4 -0.6 -0.8 -1.0

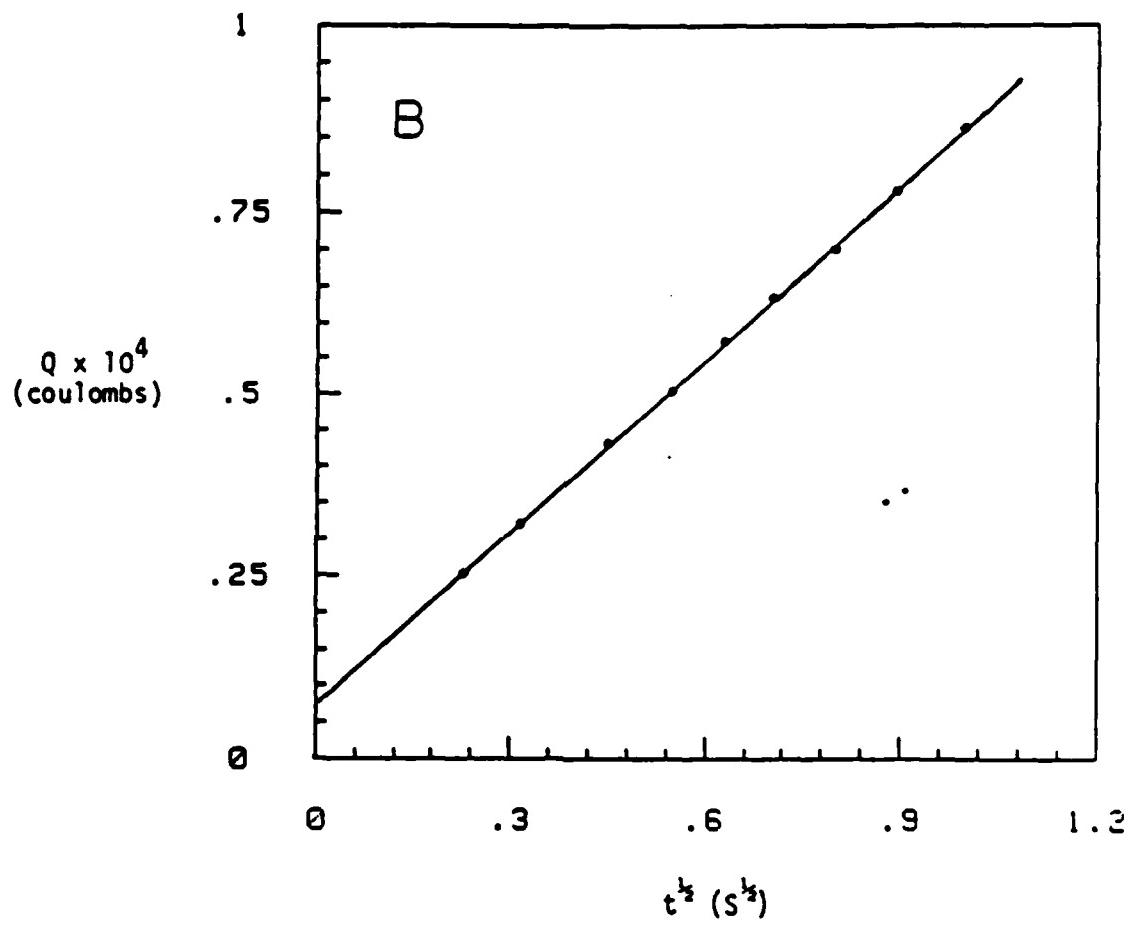
VOLTS vs SCE











TECHNICAL REPORT DISTRIBUTION LIST, GEN

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>		
Office of Naval Research Attn: Code 413 800 North Quincy Street Arlington, Virginia 22217	2	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P. O. Box 12211 Research Triangle Park, N.C. 27709	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1	Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>	
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SOO 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	1	Dr. Sam Perone Chemistry & Materials Science Department Laurence Livermore National Lab. Livermore, California 94550	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auborn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research and Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Johnson Controls 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles and Space Co., Inc. P. O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attn: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1		
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>		
Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139		Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
S. Ruby DOE (STOR) 600 E Street Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton SOH 5NH England	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. Bernard Spielvogel U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	Dr. Denton Elliott Air Force Office of Scientific Research Bolling AFB Washington, D.C. 20332	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. David Aikens Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. A. P. B. Lever Chemistry Department York University Downsview, Ontario M3J1P3 Canada	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England		Dr. Stanislaw Szpak Naval Ocean Systems Center Code 6343 San Diego, California 95152	1
Dr. A. Homy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362		Dr. Gregory Farrington Department of Materials Science and Engineering University of Pennsylvania Philadelphia, Pennsylvania 19104	
Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, D.C. 20376		Dr. Bruce Dunn Department of Engineering & Applied Science University of California Los Angeles, California 90024	

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u>	<u>Copies</u>	<u>No.</u> <u>Copies</u>	
M. L. Robertson Manager, Electrochemical and Power Sources Division Naval Weapons Support Center Crane, Indiana 47522	1	Dr. T. Marks Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1	Dr. D. Cipris Allied Corporation P. O. Box 3000R Morristown, New Jersey 07960	1
Dr. Micha Tomkiewicz Department of Physics Brooklyn College Brooklyn, New York 11210	1	Dr. M. Philpot IBM Corporation 5600 Cottle Road San Jose, California 95193	1
Dr. Lesser Blum Department of Physics University of Puerto Rico Rio Piedras, Puerto Rico 00931	1	Dr. Donald Sandstrom Washington State University Department of Physics Pullman, Washington 99164	1
Dr. Joseph Gordon, II IBM Corporation K33/281 5600 Cottle Road San Jose, California 95193	1	Dr. Carl Kanneurff Northwestern University Department of Electrical Engineering and Computer Science Evanston, Illinois 60201	1
Dr. Robert Somoano Jet Propulsion Laboratory California Institute of Technology Pasadena, California 91103	1	Dr. Edward Fletcher University of Minnesota Department of Mechanical Engineering Minneapolis, Minnesota 55455	1
Dr. Johann A. Joebstl USA Mobility Equipment R&D Command DRDME-EC Fort Belvoir, Virginia 22060	1	Dr. John Fontanella U.S. Naval Academy Department of Physics Annapolis, Maryland 21402	1
Dr. Judith H. Ambrus NASA Headquarters M.S. RTS-6 Washington, D.C. 20546	1	Dr. Martha Greenblatt Rutgers University Department of Chemistry New Brunswick, New Jersey 08903	1
Dr. Albert R. Landgrebe U.S. Department of Energy M.S. 6B025 Forrestal Building Washington, D.C. 20595	1	Dr. John Wassib Kings Mountain Specialties P. O. Box 1173 Kings Mountain, North Carolina 28086	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u>	<u>Copies</u>	N <u>Copies</u>
Dr. J. J. Brophy University of Utah Department of Physics Salt Lake City, Utah 84112	1	
Dr. Walter Roth Department of Physics State University of New York Albany, New York 12222	1	
Dr. Thomas Davis National Bureau of Standards Polymer Science and Standards Division Washington, D.C. 20234	1	
Dr. Charles Martin Department of Chemistry Texas A&M University	1	
Dr. Anthony Sammells Institute of Gas Technology 3424 South State Street Chicago, Illinois 60616	1	
Dr. H. Tachikawa Department of Chemistry Jackson State University Jackson, Mississippi 39217	1	
Dr. W. M. Risen Department of Chemistry Brown University Providence, Rhode Island	1	

MED
-8